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# Theories and Mechanisms of Adhesion

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> There are agents in nature able to make the particles of joints stick together by very strong attraction and it is the business of experimental philosophy to find them out.
> —*Sir Isaac Newton*

## I. INTRODUCTION

The adhesion phenomenon is relevant to many scientific and technological areas and has become in recent years a very important field of study. The main application of adhesion is bonding by adhesives, this technique replacing, at least partially, more classical mechanical attachment techniques such as bolting or riveting. It is considered to be competitive primarily because it allows us to save weight, to ensure a better stress distribution, and offers better aesthetics since the glue line is practically invisible. Applications of bonding by adhesives can be found in many industries, particularly in such advanced technical domains as the aeronautical and space industry, automobile manufacture, and electronics. Adhesives have also been introduced in such areas as dentistry and surgery.

Adhesive joints are not, however, the only applications of adhesion. Adhesion is involved whenever solids are brought into contact, as in coatings, paints, and varnishes; multilayered sandwiches; polymer blends; filled polymers; and composite materials. Since the final performance of these multicomponent materials depends significantly on the quality of the interface that is formed between the solids, it is understandable that a better knowledge of the adhesion phenomenon is required for practical applications.

Adhesion began to create real interest in scientific circles only about 60 years ago. At that time adhesion became a scientific subject in its own right but is still a subject in which empiricism and technology are slightly in advance of science, although the gap between theory and practice has been shortened considerably. In fact, the term *adhesion* covers a wide variety of concepts and ideas, depending on whether the subject is broached from a molecular, microscopic, or macroscopic point of view or whether one talks about formation of the interface or failure of the formed system. The term *adhesion* is therefore ambiguous, meaning both the establishment of interfacial bonds and the mechanical load required to break an assembly. As a matter of fact, one of the main difficulties in the study of adhesion mechanisms lies in the fact that the subject is at the boundary of

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several scientific fields, including macromolecular science, physical chemistry of surfaces and interfaces, materials science, mechanics and micromechanics of fracture, and rheology. Consequently, the study of adhesion uses various concepts, depending very much on one's field of expertise, and therefore treatment of the phenomena observed can be considerably different. This variety of approaches is emphasized by the fact that many theoretical models of adhesion have been proposed, which together are both complementary and contradictory:

1. Mechanical interlocking
2. Electronic theory
3. Theory of boundary layers and interphases
4. Adsorption (thermodynamic) theory
5. Diffusion theory
6. Chemical bonding theory.

Among these models, one usually distinguishes rather arbitrarily between mechanical and specific adhesion, the latter being based on the various types of bonds (electrostatic, secondary, chemical) that can develop between two solids. Actually, each of these theories is valid to some extent, depending on the nature of the solids in contact and the conditions of formation of the bonded system. Therefore, they do not negate each other and their respective importance depends largely on the system chosen.

## II. MECHANISMS OF ADHESION

### A. Mechanical Interlocking

The mechanical interlocking model, proposed by MacBain and Hopkins in 1925 [1], conceives of mechanical keying, or interlocking, of the adhesive into the cavities, pores, and asperities of the solid surface to be the major factor in determining adhesive strength. One of the most consistent examples illustrating the contribution of mechanical anchoring was given many years ago by Borroff and Wake [2], who have measured the adhesion between rubber and textile fabrics. These authors have clearly proved that penetration of the protruding fiber ends into the rubber was the most important parameter in such adhesive joints. However, the possibility of establishing good adhesion between smooth surfaces leads to the conclusion that the theory of mechanical keying cannot be considered to be universal. To overcome this difficulty, following the approach suggested primarily by Gent and Schultz [3,4], Wake [5] has proposed that the effects of both mechanical interlocking and thermodynamic interfacial interactions could be taken into account as multiplying factors for estimating the joint strength $G$:

$$G = (\text{constant}) \times (\text{mechanical keying component}) \times (\text{interfacial interactions component})$$

Therefore, according to the foregoing equation, a high level of adhesion should be achieved by improving both the surface morphology and physicochemical surface properties of substrate and adhesive. However, in most cases, the enhancement of adhesion by mechanical keying can be attributed simply to the increase in interfacial area due to surface roughness, insofar as the wetting conditions are fulfilled to permit penetration of the adhesive into pores and cavities.

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Work by Packham and co-workers [6–9] has further stressed the notable role played by the surface texture of substrates in determining the magnitude of the adhesive strength. In particular, they have found [6] that high values of peel strength of polyethylene on metallic substrates were measured when a rough and fibrous type of oxide surface was formed on the substrate. More recently, Ward et al. [10–12] have emphasized the improvement in adhesion, measured by means of a pull-out test, between plasma-treated polyethylene fibers and epoxy resin. In that case, long-time plasma treatments create a pronounced pitted structure on the polyethylene surface, which can easily be filled by the epoxy resin by means of good wetting.

One of the most important criticisms of the mechanical interlocking theory, as suggested in different studies [9,13,14], is that improved adhesion does not necessarily result from a mechanical keying mechanism but that the surface roughness can increase the energy dissipated viscoelastically or plastically around the crack tip and in the bulk of the materials during joint failure. Effectively, it is now well known that this energy loss is often the major component of adhesive strength.

## B. Electronic Theory

The electronic theory of adhesion was proposed primarily by Deryaguin and co-workers [15–19] in 1948. These authors have suggested that an electron transfer mechanism between the substrate and the adhesive, having different electronic band structures, can occur to equalize the Fermi levels. This phenomenon could induce the formation of a double electrical layer at the interface, and Deryaguin et al. have proposed that the resulting electrostatic forces can contribute significantly to the adhesive strength. Therefore, the adhesive–substrate junction can be analyzed as a capacitor. During interfacial failure of this system, separation of the two plates of the capacitor leads to an increasing potential difference until a discharge occurs. Consequently, it is considered that adhesive strength results from the attractive electrostatic forces across the electrical double layer. The energy of separation of the interface $G_e$ is therefore related to the discharge potential $V_e$ as follows:

$$G_e = \frac{h\varepsilon_d}{8\pi}\left(\frac{\partial V_e}{\partial h}\right)^2 \tag{1}$$

where $h$ is the discharge distance and $\varepsilon_d$ the dielectric constant. Moreover, according to such an approach, adhesion could vary with the pressure of the gas in which the measurement is performed. Hence Deryaguin et al. have measured, by means of a peel test, the work of adhesion at various polymer–substrate interfaces, such as poly(vinyl chloride)–glass and natural rubber–glass or steel systems, in argon and air environments at various gas pressures. A significant variation in peel energy versus gas pressure was indeed evidenced and very good agreement between the theoretical values, calculated from Eq. (1), and the measured values of $G_e$ was obtained whatever the nature of the gas used. However, several other analyses [5,20] have not confirmed these results and seem to indicate that the good agreement obtained previously was rather causal. According to Deryaguin's approach, the adhesion depends on the magnitude of the potential barrier at the substrate–adhesive interface. Although this potential barrier does exist in many cases (see, e.g., [21,22]), no clear correlation between electronic interfacial parameters and work of adhesion is usually found. Moreover, for systems constituted of glass substrate coated with a vacuum-deposited layer of gold, silver, or copper, von Harrach and Chapman [23]

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have shown that the electrostatic contribution to peel strength, estimated from the measurement of charge densities, can always be considered as negligible. Furthermore, as already mentioned, the energy dissipated viscoelastically or plastically during fracture experiments plays a major role on the measured adhesive strength, but it is not included conceptually in the electronic theory of adhesion. Finally, it could be concluded that the electrical phenomena often observed during failure processes are the consequence rather than the cause of high bond strength.

### C. Theory of Weak Boundary Layers: Concept of Interphase

It is now well known that alterations and modifications of the adhesive and/or adherend can be found in the vicinity of the interface leading to the formation of an interfacial zone exhibiting properties (or properties gradient) that differ from those of the bulk materials. The first approach to this problem is due to Bikerman [24], who stated that the cohesive strength of a weak boundary layer (WBL) can always be considered as the main factor in determining the level of adhesion, even when the failure appears to be interfacial. According to this assumption, the adhesion energy $G$ is always equal to the cohesive energy $G_c$(WBL) of the weaker interfacial layer. This theory is based primarily on probability considerations showing that the fracture should never propagate only along the adhesive–substrate interface for pure statistical reasons and that cohesive failure within the weaker material near the interface is a more favorable event. Therefore, Bikerman has proposed several types of WBLs, such as those resulting from the presence at the interface of impurities or short polymer chains.

Two main criticisms against the WBL argument can be invoked. First there is much experimental evidence which shows clearly that purely interfacial failure does occur for many different systems. Second, although the failure is cohesive in the vicinity of the interface in at least one of the materials in contact, this cannot necessarily be attributed to the existence of a WBL. According to several authors [25,26], the stress distribution in the materials and the stress concentration near the crack tip certainly imply that the failure must propagate very close to the interface, but not at the interface.

However, the creation of interfacial layers has received much attention in recent years and has led to the concept of "thick interface" or "interphase," widely used in adhesion science [27]. Such interphases are formed whatever the nature of both adhesive and substrate, their thickness being between the molecular level (a few angstroms or nanometers) and the microscopic scale (a few micrometers or more). Many physical, physicochemical, and chemical phenomena are responsible for the formation of such interphases, as shown from examples taken from our own recent work [28]:

1. The orientation of chemical groups or the overconcentration of chain ends to minimize the free energy of the interface [29]
2. Migration toward the interface of additives or low-molecular-weight fraction [30]
3. The growth of a transcrystalline structure, for example, when the substrate acts as a nucleating agent [31]
4. Formation of a pseudoglassy zone resulting from a reduction in chain mobility through strong interactions with the substrate [32]
5. Modification of the thermodynamics and/or kinetics of the polymerization or cross-linking reaction at the interface through preferential adsorption of reaction species or catalytic effects [33,34].

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It is clear that the presence of such interphases can strongly alter the strength of multicomponent materials and that the properties of these layers must not be ignored in the analysis of adhesion measurement data. A complete understanding of adhesion, allowing performance prediction, must take into account potential formation of these boundary layers.

## D. Adsorption (or Thermodynamic) Theory

The thermodynamic model of adhesion, generally attributed to Sharpe and Schonhorn [35], is certainly the most widely used approach in adhesion science at present. This theory is based on the belief that the adhesive will adhere to the substrate because of interatomic and intermolecular forces established at the interface, provided that an intimate contact is achieved. The most common interfacial forces result from van der Waals and Lewis acid–base interactions, as described below. The magnitude of these forces can generally be related to fundamental thermodynamic quantities, such as surface free energies of both adhesive and adherend. Generally, the formation of an assembly goes through a liquid–solid contact step, and therefore criteria of good adhesion become essentially criteria of good wetting, although this is a necessary but not sufficient condition.

In the first part of this section, wetting criteria as well as surface and interface free energies are defined quantitatively. The estimation of a reversible work of adhesion $W$ from the surface properties of materials in contact is therefore considered. Next, various models relating the measured adhesion strength $G$ to the free energy of adhesion $W$ are examined.

### 1. *Wetting Criteria, Surface and Interface Free Energies, and Work of Adhesion*

In a solid–liquid system, wetting equilibrium may be defined from the profile of a sessile drop on a planar solid surface. Young's equation [36], relating the surface tension $\gamma$ of materials at the three-phase contact point to the equilibrium contact angle $\theta$, is written as

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \tag{2}$$

The subscripts S, L, and V refer, respectively, to solid, liquid and vapor phases, and a combination of two of these subscripts corresponds to the given interface (e.g., SV corresponds to a solid–vapor interface). The term $\gamma_{SV}$ represents the surface free energy of the substrate after equilibrium adsorption of vapor from the liquid and is sometimes lower than the surface free energy $\gamma_S$ of the solid in vacuum. This decrease is defined as the spreading pressure $\pi$ ($\pi = \gamma_S - \gamma_{SV}$) of the vapor onto the solid surface. In most cases, in particular when dealing with polymer materials, $\pi$ could be neglected and, to a first approximation, $\gamma_S$ is used in place of $\gamma_{SV}$ in wetting analyses. When the contact angle has a finite value ($\theta > 0^\circ$), the liquid does not spread onto the solid surface. On the contrary, when $\theta = 0^\circ$, the liquid totally wets the solid and spreads over the surface spontaneously. Hence a condition for spontaneous wetting to occur is

$$\gamma_S \geq \gamma_{SL} + \gamma_{LV} \tag{3}$$

or

$$S = \gamma_S - \gamma_{SL} - \gamma_{LV} \geq 0 \tag{4}$$

the quantity $S$ being called the spreading coefficient. Consequently, Eq. (4) constitutes a wetting criterion. It is worth noting that geometrical aspects or processing conditions, such

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as surface roughness of the solid and applied external pressure, are able to restrict the applicability of this criterion.

However, a more fundamental approach leading to the definition of other wetting criteria is based on analysis of the nature of forces involved at the interface and allows calculation of the free energy of interactions between two materials to be made. For low-surface-energy solids such as polymers, many authors have estimated the thermodynamic surface free energy from contact-angle measurements. The first approach was an empirical one developed by Zisman and co-workers [37–39]. They established that a linear relationship often exists between the cosine of the contact angle, $\cos\theta$, of several liquids and their surface tension, $\gamma_{LV}$. Zisman introduced the concept of critical surface tension, $\gamma_c$, which corresponds to the value of the surface energy of an actual or hypothetical liquid that will just spread on the solid surface, giving a zero contact angle. However, there is no general agreement about the meaning of $\gamma_c$ and Zisman himself has always emphasized that $\gamma_c$ is not the surface free energy of the solid but only a closely related empirical parameter.

For solid–liquid systems, taking into account Dupré's relationship [40], the adhesion energy $W_{SL}$ is defined as

$$W_{SL} = \gamma_S + \gamma_{LV} - \gamma_{SL} = \gamma_{LV}(1 + \cos\theta) \tag{5}$$

in agreement with Eq. (2) and neglecting the spreading pressure. Fowkes [41] has proposed that the surface free energy $\gamma$ of a given entity can be represented by the sum of the contributions of different types of interactions. Schultz et al. [42] have suggested that $\gamma$ may be expressed by only two terms: a dispersive component (London's interactions) and a polar component (superscripts D and P, respectively), as follows:

$$\gamma = \gamma^D + \gamma^P \tag{6}$$

The last term on the right-hand side of this equation corresponds to all the nondispersion forces, including Debye and Keesom interactions, as well as hydrogen bonding. Fowkes [43] has also considered that the dispersive part of these interactions between solids 1 and 2 can be well quantified as twice the geometric mean of the dispersive component of the surface energy of both entities. Therefore, in the case of interactions involving only dispersion forces, the adhesion energy $W_{12}$ is given by

$$W_{12} = 2(\gamma_1^D \gamma_2^D)^{1/2} \tag{7}$$

By analogy with the work of Fowkes, Owens and Wendt [44] and then Kaelble and Uy [45] have suggested that the nondispersive part of interactions between materials can be expressed as the geometric mean of the nondispersive components of their surface energy, although there is no theoretical reason to represent all the nondispersive interactions by this type of expression. Hence the work of adhesion $W_{12}$ becomes

$$W_{12} = 2(\gamma_1^D \gamma_2^D)^{1/2} + 2(\gamma_1^P \gamma_2^P)^{1/2} \tag{8}$$

For solid–liquid equilibrium, a direct relationship between the contact angle $\theta$ of the drop of a liquid on a solid surface and the surface properties of both products is obtained from Eqs. (5) and (8). By contact-angle measurements of droplets of different liquids of known surface properties, the components $\gamma_S^D$ and $\gamma_S^P$ of the surface energy of the substrate can then be determined.

More recently, it has been shown, in particular by Fowkes and co-workers [46–49], that electron acceptor and donor interactions, according to the generalized Lewis acid–base concept, could be a major type of interfacial force between the adhesive and the

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substrate. This approach is able to take into account hydrogen bonds, which are often involved in adhesive joints. Moreover, Fowkes and Mostafa [47] have suggested that the contribution of the polar (dipole–dipole) interactions to the thermodynamic work of adhesion could generally be neglected compared to both dispersive and acid–base contributions. They have also consindered that the acid–base component $W^{ab}$ of the adhesion energy can be related to the variation of enthalpy, $-\Delta H^{ab}$, corresponding to the establishment of acid–base interactions at the interface, as follows:

$$W^{ab} = f(-\Delta H^{ab})\, n^{ab} \tag{9}$$

where $f$ is a factor that converts enthalpy into free energy and is taken equal to unity, and $n^{ab}$ is the number of acid–base bonds per unit interfacial area, close to about 6 μmol/m$^2$. Therefore, from Eqs. (7) and (9), the total work of adhesion $W_{12}$ becomes

$$W_{12} = 2(\gamma_1^D \gamma_2^D)^{1/2} + f(-\Delta H^{ab})\, n^{ab} \tag{10}$$

The experimental values of the variation of enthalpy ($-\Delta H^{ab}$) can be estimated from the work of Drago and co-workers [50,51], who proposed the following relationship:

$$-\Delta H^{ab} = C^A C^B + E^A E^B \tag{11}$$

where $C^A$ and $E^A$ are two quantities that characterize the acidic material at the interface, and similarly, $C^B$ and $E^B$ characterize the basic material. The validity of Eq. (11) was clearly evidenced for polymer adsorption on various substrates [49]. Another estimation of ($-\Delta H^{ab}$) can be carried out from the semiempirical approach defined by Gutmann [52], who has proposed that each material may be characterized by two constants: an electron acceptor number AN and an electron donor number DN. For solid surfaces, similar numbers, $K_A$ and $K_D$, respectively, have been defined and measured by inverse gas chromatography [53–55]. In this approach, the enthalpy ($-\Delta H^{ab}$) of formation of acid–base interactions at the interface between two solids 1 and 2 is now given by [52,53]

$$-\Delta H^{ab} = K_{A1} K_{D2} + K_{A2} K_{D1} \tag{12}$$

This expression was applied successfully by Schultz et al. [55] to describe fiber–matrix adhesion in the field of composite materials.

Finally, it must be mentioned that acid–base interactions can also be analyzed in terms of Pearson's hard–soft acid–base (HSAB) principle [56,57]. At present, the application of this concept to solid–solid interactions and thus to adhesion is under investigation.

### 2. *Models Relating the Adhesion Strength G to the Adhesion Energy W*

Although described also in Section II.F, these models also apply to other types of interfacial interactions. One of the most important models in adhesion science, usually called the *rheological model or model of multiplying factors*, was proposed primarily by Gent and Schultz [3,4] and then reexamined using a fracture mechanics approach by Andrews and Kinloch [58] and Maugis [59]. In this model, the peel adhesion strength is simply equal to the product of $W$ by a loss function $\Phi$, which corresponds to the energy irreversibly dissipated in viscoelastic or plastic deformations in the bulk materials and at the crack tip and depends on both peel rate $v$ and temperature $T$:

$$G = W\Phi(v, T) \tag{13}$$

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As already mentioned, the value of $\Phi$ is usually far higher than that of $W$, and the energy dissipated can then be considered as the major contribution to the adhesion strength $G$. In the case of assemblies involving elastomers, it has been clearly shown in various studies [3,4,58,60–62] that the viscoelastic losses during peel experiments, and consequently, the function $\Phi$, follow a time–temperature equivalent law such as that of Williams et al. [63].

It is more convenient to use the intrinsic fracture energy $G_0$ of the interface in place of $W$ in Eq. (13), as follows:

$$G = G_0\Phi(v, T) \tag{14}$$

Effectively, when viscoelastic losses are negligible (i.e., when performing experiments at very low peel rate or high temperature), $\Phi \rightarrow 1$ and $G$ must tend toward $W$. However, the resulting threshold value $G_0$ is generally 100 to 1000 times higher than the thermodynamic work of adhesion, $W$.

From a famous fracture analysis of weakly cross-linked rubbers called the *trumpet model*, de Gennes has derived [64] an expression similar to equation (14) when the crack propagation rate $v$ is sufficiently high. He distinguished three different regions along the trumpet starting from the crack tip: a hard, a viscous, and finally, a soft zone. The length of the hard region is equal to $v\tau$, where $\tau$ is the relaxation time, and then the viscous region extends to a distance $\lambda v\tau$. Factor $\lambda$ is the ratio of the high-frequency elastic modulus to the zero-frequency elastic modulus of the material, and obviously represents the viscoelastic behavior of the rubber. Hence according to this approach, it is shown that the total adhesive work is given by the following expression, similar to Eq. (14):

$$G \sim G_0\lambda \tag{15}$$

where $G_0$ is the intrinsic fracture energy for low velocities (i.e., when the polymer near the crack behaves as a soft material).

Carré and Schultz [65] have reexamined the significance of $G_0$ on cross-linked elastomer–aluminum assemblies and proposed that it can be expressed as

$$G_0 = Wg(M_c) \tag{16}$$

where $g$ is a function of molecular weight $M_c$ between cross-link nodes and corresponds to a molecular dissipation. Such an approach is based on Lake and Thomas's argument [66], which states that to break a chemical bond somewhere in a chain, all bonds in the chain must be stressed close to their ultimate strength. More recently, de Gennes [67] has proposed further analysis of this problem. He postulates that the main energy dissipation near the interface could be due to the extraction of short segments of chains in the junction zone during crack opening, this phenomenon being called the *suction process*. From a volume balance and a stress analysis, the following expression of the intrinsic fracture energy $G_0$ is obtained for low fracture velocity:

$$G_0 = \sigma_c a^2 vL \tag{17}$$

where $\sigma_c$ is a threshold stress that can be considered as a material constant to a first approximation, and $a^2$, $v$, and $L$ are, respectively, the cross-sectional area, the number per unit interfacial area, and the extended length of chain segments sucked out during the crack propagation. At present, no experimental verification of this approach has yet been published. Obviously, this analysis holds only for values of $L$ less than $L_e$ (i.e., the critical length at which physical entanglements between macromolecular chains just occur). The case where $L > L_e$ implies at least a disentanglement process, but above all, a process of chain scission, which is analyzed below.

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Concerning the adhesion phenomena occurring at the fiber–matrix interface in composite materials, Nardin and Schultz [68] have recently proposed that the shear strength $\tau_i$ of the interface, measured by means of a fragmentation test on single fiber composites, is related directly to the free energy of adhesion $W$, calculated from Eq. (10), according to

$$G \sim \kappa\tau_i = \left(\frac{E_m}{E_f}\right)^{1/2} W \tag{18}$$

In this expression, $\kappa$ is a constant equal to about 0.5 nm, corresponding to a mean intermolecular distance when only physical interactions (dispersive and acid–base interactions) are involved; $E_m$ and $E_f$ are the elastic moduli of the matrix and the fiber, respectively. This model is equivalent to that of Gent and Schultz [3,4] for a cylindrical geometry and in the case of pure elastic stress transfer between both materials. It is very well verified experimentally for various fiber–matrix systems. The influence of the formation of interfacial layers exhibiting mechanical behavior completely different from that of the bulk matrix has also been examined [31].

Finally, it is worth examining the analyses concerning tack, in other words, the instantaneous adhesion when a substrate and an adhesive are put in contact for a short time $t$ (of the order of 1 s) under a given pressure. This tack phenomenon is of great importance for processing involving hot-melt or pressure-sensitive adhesives. First, it has clearly been shown [69] that the viscoelastic characteristics of the adhesive, in particular its viscous modulus, play a major role on the separation energy. Recently, de Gennes [70] has suggested that the measured tack could be related to both the free adhesion energy $W$ and the rheological properties of the bulk adhesive, as follows:

$$G_{\text{tack}} \sim \begin{cases} W\dfrac{\mu_\infty}{\mu_0} & \text{for weakly cross-linked elastomers} \quad (19) \\ W\dfrac{t}{\tau} & \text{for uncross-linked elastomers} \quad (19') \end{cases}$$

where $\mu_\infty$ and $\mu_0$ are the high-frequency and zero-frequency moduli of the adhesive, respectively, and $\tau$ is the reptation time of the macromolecular chains (see the next section). The latter equation holds for time $t$ much larger than this reptation time. The experimental verification of this approach is under investigation.

## E. Diffusion Theory

The diffusion theory of adhesion is based on the assumption that the adhesion strength of polymers to themselves (autohesion) or to each other is due to mutual diffusion (interdiffusion) of macromolecules across the interface, thus creating an interphase. Such a mechanism, mainly supported by Voyutskii [71], implies that the macromolecular chains or chain segments are sufficiently mobile and mutually soluble. This is of great importance for many adhesion problems, such as healing and welding processes. Therefore, if interdiffusion phenomena are involved, the joint strength should depend on different factors, such as contact time, temperature, nature and molecular weight of polymers, and so on. Actually, such dependences are experimentally observed for many polymer–polymer junctions. Vasenin [72] has developed, from Fick's first law, a quantitative model for the diffusion theory that correlates the amount of material $w$ diffusing in a given $x$ direction across a plane of unit area to the concentration gradient $\partial c/\partial x$ and the time $t$:

$$\partial w = -D_f\, \partial t \frac{\partial c}{\partial x} \tag{20}$$

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where $D_f$ is the diffusion coefficient. To estimate the depth of penetration of the molecules that interdiffused into the junction region during the time of contact $t_c$, Vasenin assumed that the variation of the diffusion coefficient with time is of the form $D_d t_c^{-\beta}$, where $D_d$ is a constant characterizing the mobility of the polymer chains and $\beta$ is on the order of 0.5. Therefore, it is possible to deduce the depth of penetration $l_p$ as well as the number $N_c$ of chains crossing the interface, which are given by

$$l_p \sim k\,(\pi D_d t_c^{1/2})^{1/2} \tag{21}$$

$$\mathrm{N}_c = \left(\frac{2\mathrm{N}\rho}{M}\right)^{2/3} \tag{22}$$

where $k$ is a constant, N is Avogadro's number, and $\rho$ and $M$ are, respectively, the density and the molecular weight of the polymer. Finally, Vasenin assumed that the measured peel energy $G$ was proportional to both the depth of penetration and the number of chains crossing the interface between the adhesive and the substrate. From Eqs. (21) and (22), $G$ becomes

$$G \sim K\left(\frac{2\mathrm{N}\rho}{M}\right)^{2/3} D_d^{1/2} t_c^{1/4} \tag{23}$$

where $K$ is a constant that depends on molecular characteristics of the polymers in contact, Experimental results and theoretical predictions from Eq. (23) were found [72] in very good agreement in the case of junctions between polyisobutylenes of different molecular weights. In particular, the dependence of $G$ on $t_c^{1/4}$ and $M^{-2/3}$ was clearly evidenced.

One important criticism of the model proposed by Vasenin is that the energy dissipated viscoelastically or plastically during peel measurements does not appear in Eq. (23). Nevertheless, in his work, the values of coefficients $K$ and $D_d$ are not theoretically quantified but determined only by fitting. Therefore, it can be assumed that the contribution of hysteretic losses to the peel energy is implicitly included in these constants.

In fact, the major scientific aspect of interdiffusion phenomena is concerned with the dynamics of polymer chains in the interfacial region. Recently, the fundamental understanding of the molecular dynamics of entangled polymers has advanced significantly due to the theoretical approach proposed by de Gennes [73], extended later by Doi and Edwards [74] and Graessley [75]. This new approach stems from the idea that the chains cannot pass through each other in a concentrated polymer solution, a melt, or a solid polymer. Therefore, a chain with a random coil conformation is trapped in an environment of fixed obstacles. This constraint confines each chain inside a tube. De Gennes has analyzed the motion, limited mainly to effective one-dimensional diffusion along a given path, of a polymer chain subjected to such a confinement. He described this type of motion as wormlike and gave it the name *reptation*. The reptation relaxation time $\tau$ associated with the movement of the center of gravity of the entire chain through the polymer was found to vary with the molecular weight $M$ as $M^3$. Moreover, the diffusion coefficient $D$, which defines the diffusion of the center of mass of the chain, takes the form $D \sim M^{-2}$.

One of the most important and useful applications of the reptation concept concerns crack healing, which is primarily the result of the diffusion of macromolecules across the interface. This healing process was studied particularly by Kausch and co-workers [76]. The problem of healing is to correlate the macroscopic strength measurements to the microscopic description of motion. The difference between self-diffusion phenomena in the bulk polymer and healing is that the polymer chains in the former case move over

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distances many times larger than their gyration radii, whereas in the latter case, healing is essentially complete in terms of joint strength in the time that a macromolecule initially close to the interface needs to move about halfway across this interface. This problem was analyzed by several authors, who have considered that the healing process is controlled by different factors, such as (1) the number of bridges across the interface for de Gennes [77], (2) the crossing density of molecular contacts or bridges for Prager and Tirrell [78], (3) the center-of-mass Fickian interdiffusion distance for Jud et al. [76], and (4) the monomer segment interpenetration distance for Kim and Wool [79]. The resulting scaling laws for the fracture energy versus time $t$ during healing are the following:

$$G \sim \begin{cases} t^{1/2}M^{-3/2} & \text{for (1) and (2)} \quad (24) \\ t^{1/2}M^{-1} & \text{for (3)} \quad (24') \\ t^{1/2}M^{-1/2} & \text{for (4)} \quad (24'') \end{cases}$$

If there are some differences in the exponent of the molecular weight in these expressions, all the approaches agree with the dependence of $G$ on the square root of healing time, such a dependence having been clearly evidenced experimentally for poly(methyl methacrylate) polymer, for example [76], in contradiction with Vasenin's model.

Finally, it can be concluded that diffusion phenomena do actually contribute greatly to the adhesive strength in many cases involving polymer–polymer junctions. Nevertheless, the interdiffusion of macromolecular chains requires both polymers to be sufficiently soluble and the chains to possess a sufficient mobility. These conditions are obviously fulfilled for autohesion, healing, or welding of identical polymers processes. However, diffusion can become a most unlikely mechanism if the polymers are not or only slightly soluble, if they are highly cross-linked or crystalline, or put in contact at temperatures far below their glass transition temperature. Nevertheless, in the case of junctions between two immiscible polymers, the interface could be strengthened by the presence of a diblock copolymer, in which each molecule consists of a block of the first polymer bonded to a block of the second polymer, or each of the two blocks is miscible with one of the polymers. The copolymer molecules concentrate generally at the interface and each block diffuses or "dissolves" into the corresponding polymer. Therefore, the improvement in joint strength can also be related to an interdiffusion process. When the molecular weight $M$ of each block of the copolymer is inferior to the critical entanglement weight $M_e$ for which entanglements of chains just occur in the polymer, the adhesion strength could be interpreted in terms of the suction mechanism described in Section II.D. On the contrary, when $M > M_e$, the failure of the joint generally requires the rupture of the copolymer chains. The latter phenomenon (i.e., chain scission or more precisely rupture of chemical bonds) is analyzed in the next section.

## F. Chemical Bonding Theory

It is easily understandable that chemical bonds formed across the adhesive–substrate interface can greatly participate to the level of adhesion between both materials. These bonds are generally considered as primary bonds in comparison with physical interactions, such as van der Waals, which are called *secondary force interactions*. The terms *primary* and *secondary* stem from the relative strength or bond energy of each type of interaction. The typical strength of a covalent bond, for example, is on the order of 100 to 1000 kJ/mol, whereas those of van der Waals interactions and hydrogen bonds do not exceed 50 kJ/mol. It is clear that the formation of chemical bonds depends on the reactivity of both adhesive

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and substrate. Different types of primary bonds, such as ionic and covalent bonds, at various interfaces have been evidenced and reported in the literature. The most famous example concerns the bonding to brass of rubber cured with sulfur, adhesion resulting from the creation of polysulfide bonds [80]. One of the most important adhesion fields involving interfacial chemical bonds is the use of adhesion promoter molecules, generally called *coupling agents*, to improve the joint strength between adhesive and substrate. These species are able to react chemically on both ends, with the substrate on the one side and the polymer on the other, thus creating a chemical bridge at the interface. The coupling agents based on silane molecules are the most common type of adhesion promoters [81]. They are widely employed in systems involving glass or silica substrates, and more particularly in the case of polymer-based composites reinforced by glass fibers. In addition to the improvement in joint strength, an important enhancement of the environmental resistance of the interface, in particular to moisture, can be achieved in the presence of such coupling agents.

The influence of chemical bonds on the joint strength $G$, and more precisely on the intrinsic adhesion fracture energy $G_0$, defined earlier, has been analyzed in several studies. The most relevant and elegant work in this area was performed by Gent and Ahagon [82], who have examined the effect on the adhesion of polybutadiene to glass of chemical bonds established at the interface by using silane coupling agents. In these experiments the surface density of interfacial covalent bonds between the glass substrate and the cross-linked elastomer was varied by treating the glass plates with different mixtures of vinyl- and ethyl-terminated silanes. Obviously, both species form siloxane bonds on the glass surface. Moreover, it was assumed that the vinylsilane can react chemically with the polybutadiene during the cross-linking treatment of this rubber, where a radical reaction is involved. On the contrary, a chemical reaction between the ethyl group of the latter silane and the elastomer is unlikely. Therefore, Gent and Ahagon [82] have shown that the intrinsic peel energy $G_0$ increases linearly with the surface concentration of vinylsilane, in good agreement with their assumptions, and thus proved the important effect of primary bonds on adhesive strength.

Another experimental evidence of the chemical bond effect on the interfacial strength is relative to the adhesion between two sheets of cross-linked polyethylene [83]. To control the number of chemical bonds at the interface, the assemblies were prepared as follows. First, polyethylene containing 2% by weight of dicumylperoxide (DCP) was molded into sheets at rather low temperature (120°C) to prevent the decomposition of DCP. Second, partial pre-cross-linking of the two separate polymer sheets was performed at 140°C for a given time. Since the decomposition kinetics of DCP is known at this temperature, the degree of cross-linking can be varied as a function of time. Finally, assemblies of the two resulting sheets are obtained under pressure by heating at 180°C to ensure the total decomposition of DCP. Hence this technique leads to complete cross-linking in the bulk of the assembly, the mechanical properties of which therefore remain constant, whereas the surface density of interfacial bonding can be varied. In agreement with previous results obtained by Gent and Ahagon [82], a linear relationship has been established between the peel energy $G$ and the number of bonds $v$ per unit interfacial area, insofar as $v$ does not exceed $1 \times 10^{13}$ bonds/cm$^2$.

More recently, in a series of papers [84–86], Brown has analyzed the improvement in adhesion between two immiscible polymers [i.e., poly(methyl methacrylate) (PMMA) and polyphenylene oxide (PPO)] by the presence of polystyrene–PMMA diblock copolymers. Since one of the blocks is PMMA and the other is polystyrene (PS), which is totally miscible with PPO, it was reasonably expected that the copolymer organizes at the

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interface, due to the fact that each block dissolves in the respective homopolymer. The molecular weight of these blocks is always superior to the critical molecular weight $M_e$, for which entanglements of chains occur in the homopolymers. Experimentally, Brown employed partially or fully deuterated copolymers in order to be able to determine the deuterium on the fracture surface after separation by secondary-ion mass spectrometry (SIMS) and forward-recoil spectroscopy (FRES) [85]. A scission of the copolymer chains near the junction point of both blocks is observed, indicating that the diblock copolymers are well organized at the interface, whatever their molecular weights, with their junction accurately located at the PMMA–PPO interface. Moreover, Brown has proposed [86] a molecular interpretation of the toughness of glassy polymers, which can also be applied to the failure of interfaces between immiscible polymers. This approach stems from the idea that the cross-tie fibrils, which exist between primary fibrils in all crazes, can transfer mechanical stress between the broken and unbroken fibrils and thus strongly affect the failure mechanics of a craze. It is based on a simple model of crack tip stress concentration. Finally, assuming that all the effectively entangled chains in the material are drawn into the fibril, the fracture energy $G$ of a polymer is found to be directly related to the square of both the areal density $v$ of entangled chains and the force $f$ required to break a polymer chain:

$$G \sim v^2 f^2 \frac{D}{S} \tag{25}$$

where $D$ is the fibril diameter and $S$ is the stress at the craze–bulk interface, which is assumed to be constant. Brown has considered [86] that diblock copolymer-coupled interfaces between PMMA and PPO are ideal experimental systems for testing the validity of his model. Indeed, a linear dependence of the interfacial fracture energy $G$ on the diblock copolymer surface density $v$, in logarithmic scales, is observed for copolymers of different molecular weights. A slope of $1.9 \pm 0.2$ was found for the master straight line in good agreement with Eq. (25). Nevertheless, it is worth noting that Brown's results involving chain scission at the interface and leading to a dependence of $G$ on $v^2$ are in contradiction with both previous examples, where linear relationships between $G$ and $v$ are established.

## III. CONCLUDING REMARKS

Adhesion is a very complex field beyond the reach of any single model or theory. Given the number of phenomena involved in adhesion, the variety of materials to be bonded, and the diversity of bonding conditions, the search for a unique, universal theory capable of explaining all the experimental facts is useless. In practice, several adhesion mechanisms can be involved simultaneously. However, it is generally assumed that the adsorption or thermodynamic theory defines the main mechanism exhibiting the widest applicability. It describes the achievement of intimate contact and the development of physical forces at the interface. This is a necessary step for interlocking, interdiffusion, and chemical bonding mechanisms to occur subsequently, further increasing the adhesive strength.

Finally, one can consider that the measured adhesive strength of an assembly could be expressed as a function of three terms relating, respectively, to (1) the interfacial molecular interactions, (2) the mechanical and rheological properties of bulk materials, and (3) the characteristics of the interphase. The first two terms have received a great deal of attention during recent decades, as a result of studies in the physical chemistry of surfaces and fracture mechanics. The third term constitutes the real challenge for a proper and complete understanding of adhesion.

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